TPD STUDY ON SO_2 GASIFICATION OF COAL CHAR

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INTRODUCTION

Elementary sulfur can be recovered from SO_2-containing gas by a gasification reaction between carbon and SO_2. Limited studies on the reaction of coal with SO_2 have been reported[1), 2)]. Works on the mechanism of gasification of coal chars with oxygen-containing gases such as O_2, H_2O, CO_2 have been carried out for a long time. Recently, many temperature-programed desorption (TPD) studies on the surface complexes formed by the chemisorption of oxygen-containing gases on carbon have been performed, because the technique is very useful to evaluate the surface active sites in detail. We already investigated the effects of coal type, mineral matter and catalyst addition on the SO_2 gasification rate of coal chars[3)]. In this study, nine coal chars derived from coals ranging from brown coal to anthracite, three demineralized coal chars and catalyst-loaded coal chars were chemisorbed with SO_2. TPD patterns of samples were obtained and the relationship between the reactivities of chars and the TPD patterns was discussed. The comparison of TPD pattern of SO_2-chemisorbed char with that of O_2-chemisorbed char was also performed.

EXPERIMENTAL

Sample

Nine coals were used in this study. Carbon contents of nine coals are as follows; Loy Yang (LY) 65.1, Yallourn (YL) 66.1, Morwell (MW) 67.9, Sufco (SF) 73.9, Taiheiyo (TH) 77.0, Leopold (LP) 79.9, Liddell (LD) 83.5, Smokyriver (SR) 90.6, Kuznetsky (KN) 90.7 (wt%, daf). The analyses of these coals have been described elsewhere[3)]. The particle size of coal was 32-60 mesh. To examine the effect of the inherent mineral matter on the reactivity and TPD pattern of char, YL, MW and TH coals were treated with a dilute HCl solution for 2 h.

Method of catalyst addition

Yallourn coal, Australian brown coal, was used for catalytic gasification experiments. Potassium carbonate, sodium hydroxide, calcium hydroxide, magnesium hydroxide and iron nitrate were used as the starting materials for catalyst impregnation. Yallourn coal treated with a dilute HCl solution was impregnated with an aqueous solution of catalyst salt and dried at 107°C. The metal to coal ratio was ranged from 1:10 to 1:200 by weight.

Reactivity measurement

The gasification reaction was conducted in a thermo-balance (Shinku-Riko, TGD-7000). The temperature was raised to the gasification temperature at a rate of 60 °C/min after evacuation and substitution with nitrogen gas. After a stationary condition was established, SO_2-N_2 gas (SO_2 concentration:5.2vol%) was introduced and the gasification of char was initiated. The isothermal reaction was allowed to continue for 2 - 10 h.

TPD experiment

TPD experiments were carried out in a fixed bed reactor with gas analysis systems. About 100mg of coal sample was placed in the fixed bed reactor and heated up to 950°C at a heating rate of 60°C/min with flowing Ar gas. The devolatilization of sample was allowed to continue for 30min. Then, two kinds of chemisorption procedures were performed as follows. Procedure 1: samples were cooled down to 150°C and then exposed to either SO_2 (5.2vol%) or O_2 (20vol%) for 60min. Procedure 2: the sample was cooled down to 800°C. Then, SO_2 gas was introduced in the reactor and the sample was cooled down to 500°C at a cooling rate of 60°C/min with flowing SO_2/Ar gas. During the adsorption stage, a part of char (less than 10% of conversion) was gasified. After evacuation and substitution with Ar gas, the samples were heated up to 900°C or 950°C at a heating rate of 5°C/min or 10°C/min under Ar flow. The gases desorbed during the heat-treatment were continuously analysed with quadrupole mass spectrometer (Nichiden Anelva AQA-200) and the total amounts of CO and CO_2 gases evolved were analysed with a gas chromatography and IR gas analysers.

RESULTS AND DISCUSSION

TPD patterns of SO_2- and O_2-chemisorbed MW chars

The TPD patterns of SO_2- and O_2-chemisorbed MW char prepared by procedure 1 are shown in Figures 1 and 2. The TPD pattern strongly depended on the type of adsorbed gas. A broad desorption of CO_2 for O_2-chemisorbed char was obtained in the range from 150°C to 650°C as previously reported by Zhang et al.[4]. On the other hand, a sharp desorption peak of CO_2 for SO_2-sorbed char appeared at around 700°C. Relatively broad desorption of CO for O_2-sorbed char was observed, while CO gas was evolved at higher temperature range for SO_2-sorbed char. It is noteworthy that no desorptions of both CO_2 and CO for SO_2-sorbed char were detected at a low temperature range below 450°C.

Reactivities and TPD patterns of raw coal chars

Figure 3 shows TG curves obtained for nine coal chars. The sample weight gradually increased in the earlier gasification stage, and then decreased. The increase in weight may be due to the adsorption of SO_2 gas to char surface and to the reaction between mineral matter in char and SO_2. The weight decrease is due to the SO_2 gasification of coal char. The reactivity and the gasification profile strongly depended on coal type. The reactivities of chars derived from coals with carbon content >80 wt% were small and those of lower-rank coal chars were high and widely spread. These results are quite similar to those obtained in the study on the steam gasification of coal chars[5]. The TPD patterns for nine coal chars prepared by procedure 2 were obtained. Four examples are shown in Figure 4. The TPD pattern depended on the coal type. A large and sharp CO_2 peak at around 700°C for MW char and YL char was observed. TH char gave a small CO_2 peak. Little CO_2 gas desorption for LP char was obtained. The TPD patterns for higher rank coal chars such as KN, SR and LD were quite similar to that of LP char. A broad desorption of CO was observed for all coal chars examined. The correlation between the reactivity and the amount of gases desorbed was examined. It was found that the amount of CO desorbed shows a good correlation with the gasification reactivity.

Effect of mineral matter on reactivity and TPD pattern

The effect of acid treatment on the reactivity and TPD profile was examined. The results are shown in Figures 5 and 6. Extraction of coal samples with HCl solution caused appreciable decrease in gasification rate, almost complete disappearance of CO_2 desorption peak and considerable decrease in CO desorption peak. Ratcliffe et al. have reported that acid treatments of lignite caused a decrease in SO_2 gasification rate of char[1]. It is well known that exchangeable cations such as Na and Ca show high activity for steam gasification of low rank coal chars[5]. The decreases in the rate and the amount of gases desorbed may be due to the removal of catalyst metals in mineral matter.

Effect of catalyst addition on reactivity and TPD pattern

The effect of catalyst addition on the reactivity and TPD pattern was investigated (Figures 7 and 8). The gasification profile and TPD pattern was strongly affected by the catalyst addition. The addition of alkaline metals such as K and Na enormously enhanced not only the gasification rate but also the amount of gases desorbed. Relatively sharp desorption peaks of CO_2 and CO for alkaline metal-loaded chars were observed at around 780°C and 830°C, respectively. Both the reactivity and the amount of gases evolved depended on the potassium loading (Figures 7 and 9). In the case of Ca catalyst, although the CO_2 desorption peak at 700°C was increased, the effectiveness of Ca as catalysts for SO_2 gasification of char was quite small. The results show that all CO_2 evolved are not responsible for the gasification rate. XRD measurements of Ca-loaded char showed that Ca catalyst was gradually transformed to CaS during SO_2 gasification of char. The TPD results obtained in this study give the information of initial reactivity of Ca-loaded char. Further investigations are needed to reveal the relationship among the TPD pattern of Ca-loaded char, the activity and chemical form of Ca catalyst.

CONCLUSIONS

The TPD patterns of coal chars chemisorbed with SO_2 gas were determined. The TPD pattern depended on the coal type, mineral matter and catalyst type. Alkaline metals such as Na and K enormously enhanced the gasification rate and the amount of CO_2 and CO evolved. A relatively good correlation was obtained between the reactivity of char and the amount of CO gas desorbed during TPD.

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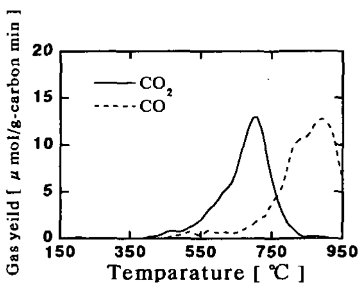

Fig.1 TPD pattern of SO_2-chemisorbed MW char.

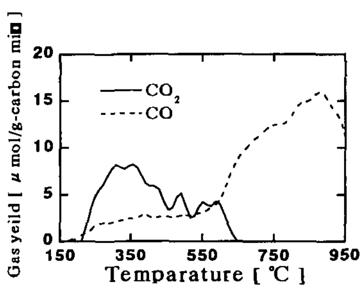

Fig.2 TPD pattern of O_2-chemisorbed MW char.

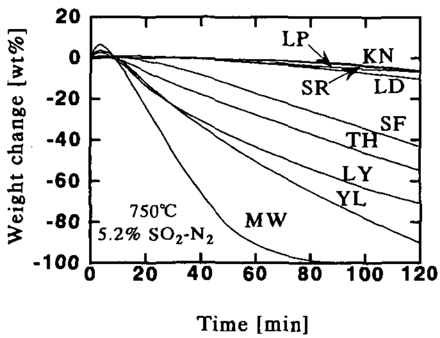

Fig.3 SO_2 gasification profiles of raw coal chars at 750℃.

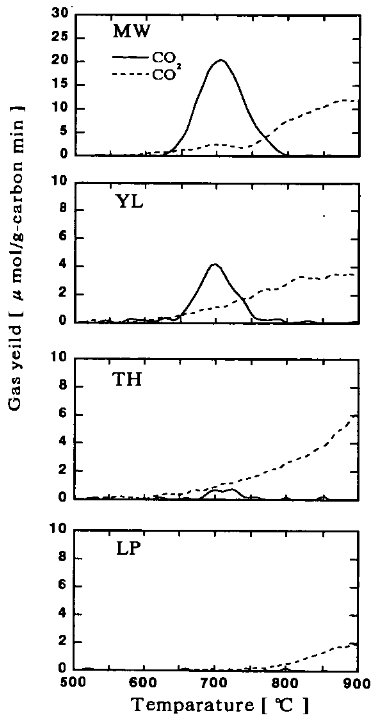

Fig.4 TPD patterns of raw coal chars.

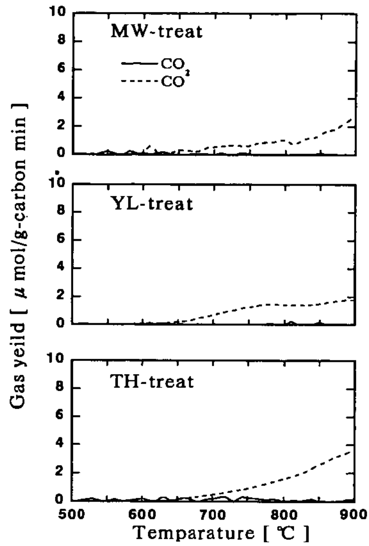

Fig.5 TPD patterns of demineralized coal chars.

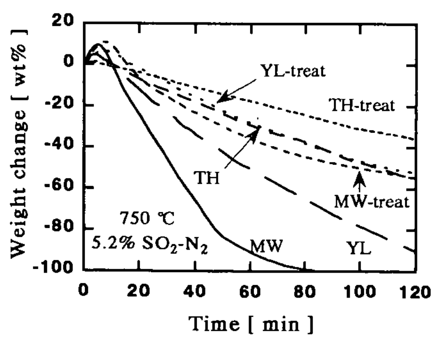

Fig.6 Effect of acid treatment on SO_2 gasification profile at 750℃.

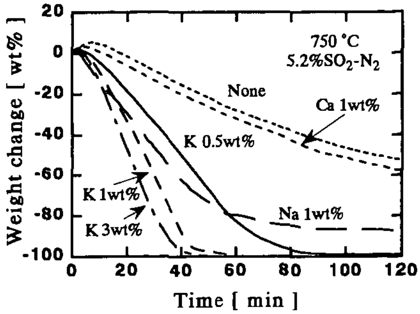

Fig.7 Catalytic SO_2 gasification of YL char at 750℃.

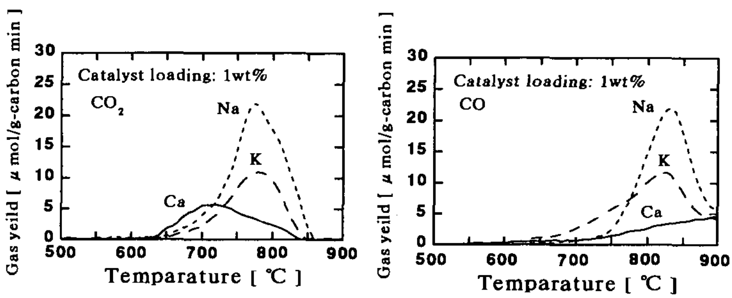

Fig.8 TPD patterns of catalyst-loaded YL chars.

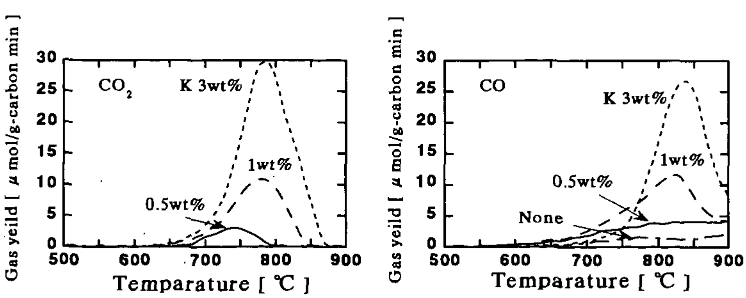

Fig.9 TPD patterns of K-loaded YL chars.

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